

William Louis CULBERSON* & Chicita F. CULBERSON* :
***Ramalina asahinae*, a new boninic acid-producing
species from Mexico****

W. L. カルバーソン*・C. F. カルバーソン* : ポニン酸
を含むメキシコ産カラタチゴケ属の 1 新種**

In 1938 Professor Yasuhiko Asahina (1938a) described *Ramalina boninensis*, the first lichen species known to produce the orcinol *meta*-depside boninic acid. He and Kusaka (1937) had determined the structure and synthesized boninic acid the year before. In the some 40 years since these papers were published, the only additional boninic acid-producing lichen reported was the new species *Cladonia humboldtii* (des Abbayes, 1961), the chemical identification having been made by Asahina. The present paper concerns the occurrence of boninic acid in two Mexican species of *Ramalina*, one of which is new and is named in honor of the late Professor Asahina.

***Ramalina asahinae* W. Culb. et C. Culb., sp. nov.**

A *R. farinacea* et speciebus affinis materia chemica medullae differt; medulla acidum boninicum continens. Apothecia et pycnidia ignota.

Mexico. Chiapas: 11 km west of San Cristóbal las Casas. On *Quercus* sp. Elev. ca. 2154 m. 28.XII.1975. W.L. Culberson 16,538 & C.F. Culberson (DUKE, holotypus). The same, on *Quercus* sp. (a different tree), W.L. Culberson 16,539, 16,540 & C.F. Culberson (DUKE).

Chemistry: Usnic acid, boninic acid, a homologue of boninic acid (probably 2-O-methylsekikaic acid), ramalinolic acid (trace), an unidentified orcinol *meta*-depside, and, as an accessory in one specimen (16,540), variolaric acid.

Ramalina asahinae belongs to the *R. farinacea* group and very closely resembles typical sorediate, sterile European specimens of that complex. It is the first member of the group known to produce orcinol rather than β -orcinol medullary products and is consequently very different chemically from the known species in the complex. In Europe the *R. farinacea* group

* Department of Botany, Duke University, Durham, NC 27706, U.S.A.

** Contribution in honor of the late Dr. Yasuhiko Asahina

includes species that produce as major medullary constituents the β -orcinol depsidones protocetraric acid (*R. farinacea* (L.) Ach. sen. str.), norstictic acid (*R. subfarinacea* (Nyl. ex Cromb.) Nyl.), norstictic and salazinic acids (*R. reagens* (B. de Lesd.) W. Culb.), and hypoprotocetraric acid (*R. hypoprotocetrarica* W. Culb.) (W. L. Culberson, 1966).

The identification of boninic acid here is based upon the study of a small specimen of *R. boninensis* (det. Magnusson) from the type locality (Wright s. n., Bonin Islands, US). By thin-layer chromatography (TLC) this specimen was found to contain usnic acid, a trace of atranorin, and three unidentified substances. Since the extract showed the typical crystals of boninic acid in the GE solution (Asahina & Kusaka, 1937; Asahina, 1938b), one of the three unidentified substances detected by TLC must be boninic acid. Two compounds have high R_f values of the sort that would be expected for boninic acid and are a pair of homologous *meta*-depsides. Boninic acid in *R. boninensis* is accompanied by a new and homologous *meta*-depside that is probably the lower homologue 2-O-methylsekikaic acid. The third substance gives an orange-brown spot very similar to that of ramalinolic acid but with lower R_f values. This compound is probably 4'-O-demethylsekikaic acid, which is the lower homologue of ramalinolic acid and the acid form of scrobiculin. (A thermal degradation experiment on this second new compound in *R. asahinae* allowed the TLC identification of decarboxylated divaricatinic acid (5-methoxy-3-propylphenol) as a decomposition product, giving strong evidence for a mono-O-methylated A ring with a three-carbon side chain.) All three medullary products found in *R. boninensis* were also identified in *R. asahinae*. A trace of the *meta*-depside ramalinolic acid is also present. One of the three specimens (16,540) contained the orcinol depsidone, variolaric acid, a very rare substance among macrolichens and one not previously reported for the genus *Ramalina*.

The same chemistry observed in *R. boninensis* and in *R. asahinae* (but without variolaric acid) was also found in an isotype (Rundel 5046, DUKE) of *R. sinaloensis* Bowl. et Rund. from Sinaloa, Mexico. The latter species was reported (Bowler & Rundel, 1972) to contain "sekikaic (?) and an unknown acid."

Boninic acid and its homologue give spots by the standardized TLC method (C. F. Culberson, 1972) that show a brownish purple color when

sprayed with 10% H_2SO_4 and heated. The standardized Rf values for the higher homologue (probably boninic acid) are 44/42, 80 in solvent A (Rf class 4), 38/29, 70 in solvent B (Rf class 5), and 62/30, 88 in solvent C (Rf class 5-6). The values for the lower homologue (probably 2-O-methylsekikaic acid) are 41/42, 80 in solvent A (Rf class 4), 35/29, 70 in solvent B (Rf class 5), and 56/30, 88 in solvent C (Rf class 5-6). The third medullary constituent (probably 4'-O-demethylsekikaic acid), with an orange-brown color on sprayed and heated plates, has standardized Rf values of 24/42, 80 in solvent A (Rf class 3), 31/29, 70 in solvent B (Rf class 4-5), and 20/30, 88 in solvent C (Rf class 3). The standardized Rf values for a trace constituent, probably ramalinolic acid, are 35/41, 82 in solvent A (Rf class 3), 41/31, 75 in solvent B (Rf class 5), and 31/31, 86 in solvent C (Rf class 4).

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朝比奈泰彦博士は 1938 年にボニン酸を含む地衣として *Ramalina boninensis* を記載したが、ここではメキシコ産の 2 種のカラタチゴケ、*R. asahinae* (新種) と *R. sinaloensis* Bowl. et. Rund. にボニン酸が含まれることを報告した。